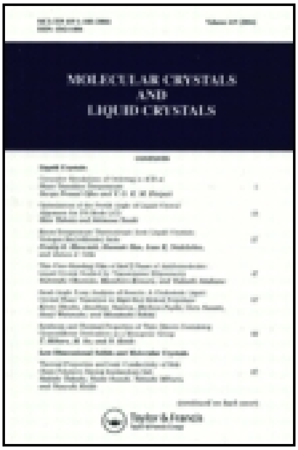

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Nuclear Magnetic Resonance in Liquid Crystal Solvents

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Abstract—Since the discovery by Saupe and Englert that a nematic phase is a satisfactory solvent for high resolution nuclear magnetic resonance (NMR) studies, the variety of liquid crystal phases which have been found useful in NMR experiments has greatly increased. The resonance studies have increased our understanding of the structure of the solvent mesophases, and of their interactions with solute molecules.

A new method to determine accurate molecular structures by the analysis of solute NMR spectra has been developed. Application to bicyclobutane will be discussed. As a side benefit, one finds other information of interest to magnetic resonance spectroscopists including the absolute values of indirect spin-spin couplings and their assignment to nuclear pairs.

Introduction

The subject of this lecture is nuclear magnetic resonance in liquid crystals. In particular, we shall review proton NMR of molecules dissolved in liquid crystal solvents. For background material we refer the reader to a number of recent reviews.[1,2]

The earliest published studies of a liquid crystal system by NMR were made in 1952 by Spence, Moses and Jain[3] on the nematic phase of para-azoxyanisole. They found a spectrum of three broad peaks spread over 3.3 gauss. The structure of the spectrum was soon explained in terms of direct dipole-dipole interactions of protons in the oriented molecules.[4] Extensive early NMR studies of pure mesophases, including the smectic phase, were made by Lippmann and Weber.[5]

A new field of study of the NMR of solute molecules in liquid crystal solvents was opened in 1963 with the publication by Saupe and Englert of the lower spectrum shown in Fig. 1.[6] This spectrum shows the proton NMR of benzene in nematic *p,p′*-di-*n*-hexyloxy-azoxybenzene. Saupe and Englert interpreted the structure of the spectrum as due to the direct magnetic dipole-dipole interaction. They also discussed the large amount of information on molecular motion, molecular structure, and magnetic resonance parameters obtainable by the analysis and interpretation of such spectra. In the same paper they published the upper spectrum of Fig. 1, which shows the high resolution proton NMR of *p*-azoxyanisole in its nematic phase.

In this paper we shall review what can be learned about the solvent mesophase from the solute spectrum, and then what can be learned about the solute. The emphasis of our work has been on developing methods to determine molecular structure. But in these studies we have also gained some information on the nature of the solvent mesophase.

NMR in Liquid Crystals

After the first observations of nuclear magnetic resonance in 1946, development was rapid, and high resolution NMR in normal (isotropic) liquids is now a standard tool in chemistry. We shall here assume that the reader has some familiarity with its basic principles.[2] Very briefly, a high resolution NMR spectrum consists of a set of narrow peaks, each representing a nuclear magnetic resonance frequency. A spectrum interpretation, that is a calculation of the peak positions and intensities, can be made in terms of the frequencies of the individual nuclei (chemical shifts) and the electron-coupled nuclear interactions (indirect coupling constants). For protons in diamagnetic materials the chemical shifts range up to a few parts per million (i.e., a few hundred Hz at 100 MHz), while the indirect couplings range up to about 15 Hz. These quantities can, however, be much larger for heavier nuclei.

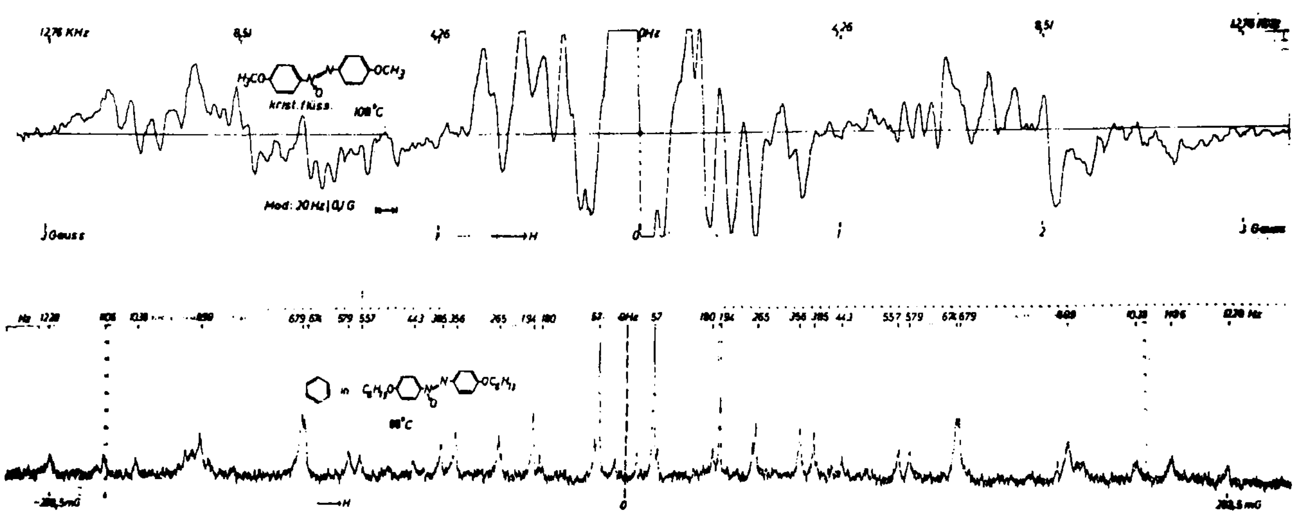

Figure 1. The upper spectrum is the proton NMR of *p*-azoxyanisole in the nematic phases. The lower spectrum is the proton NMR of benzene in nematic *p,p*′-di-*n*-hexyloxyazoxybenzene. (From: Saupe and Englert, *Phys. Rev. Letters* **11**, 463 (1963).)

NMR spectroscopy in liquid crystals differs from that in normal liquids in one basic aspect: In normal liquids the direct magnetic interactions between nuclei can be disregarded in calculations of the peak positions and intensities. Chemists using NMR as a routine analytical tool hardly give the direct interactions a thought. In liquid crystals, on the other hand, the direct interactions are the major factor determining the structure of the spectrum. At the root of this difference is the anisotropy of the liquid crystalline phase. In order to explain the relation a short discussion of the direct interaction is in order. For ease of exposition we shall refer to protons only, but most of the conclusions apply to other nuclei as well.

The physics of the direct interaction is simple: Each proton has a magnetic dipole and thus produces a magnetic field which interacts with the magnetic dipoles of the other protons in the molecule. A simple magnetostatic calculation of the interaction energy between two parallel dipoles gives that it is proportional to $(3\cos^2\theta - 1)r^{-3}$, where r is the distance between the nuclear pair and θ is the angle between the direction of the dipoles and a vector connecting the nuclei. In liquids rapid molecular tumbling occurs, and the above angular factor must be averaged over all values of θ, properly weighted. In isotropic liquids the result of this averaging process is zero and the direct coupling is absent. In liquid crystal solvents, the environment of a molecule is anisotropic, and thus different molecular orientations are no longer equally probable. The weighted average now required for the angular factor will no longer be zero. Note that only the intramolecular interactions (within a molecule) are non-zero; the intermolecular interactions (between nuclei in different molecules) still average to zero, as in isotropic liquids, and in contrast to solids where both intra- and intermolecular interactions are effective.

The strong dependence of the direct interaction on internuclear distance and orientation provides the possibility of molecular structure determination. For a completely oriented pair of protons separated by 1 Å the direct dipolar coupling fields correspond to a shift of resonant frequency of order 100,000 Hz, as degrees of orientation of 10% and higher are common, the direct interaction is often much larger than the indirect interactions and the chemical shifts.

In order to get resolved NMR spectra, a uniform alignment over the whole NMR sample is required. The diamagnetic anisotropy of the liquid crystalline phase provides the force by which a magnetic field may uniformly align the solvent.

The above considerations apply not only to the liquid crystal molecules, but also to molecules dissolved in a liquid crystal solvent. If the solute molecule is elongated (i.e., has a lower symmetry than cubic), it too will be partially oriented. Typically direct proton interactions up to about 5000 Hz are observed in solute molecules. These shifts are usually far greater than those due to chemical shifts and indirect coupling. Thus the magnetic fields due to the direct magnetic dipole-dipole coupling of nuclei determine the major structure of these NMR spectra.

Quantitative Formulation

These qualitative ideas are expressed quantitatively in the spin Hamiltonian,[7] which, expressed in frequency units, is written as follows:

$$H = \sum_{i} \gamma_i \mathscr{H}_0 (1 - \sigma_i) I_{zi} + \sum_{i>j} J_{ij} (I_{xi} I_{xj} + I_{yi} I_{yj} + I_{zi} I_{zj})$$
$$+ \sum_{i>j} D_{ij} (- \tfrac{1}{2} I_{xi} I_{xj} - \tfrac{1}{2} I_{yi} I_{yj} + I_{zi} I_{zj})$$

The first term at the right hand side represents the Zeeman energy. Here $\mathscr{H}_0$ is the applied magnetic field, γ_i the magnetogyric ratio, σ_i the screening constant (relative chemical shift) and I_{xi}, I_{yi}, I_{zi} the components of angular momentum operator of the i-th nucleus. The second term accounts for the indirect spin-spin interactions, characterized by the coupling constants J_{ij} between the i-th and j-th nuclei. The first two terms are all that are needed in the interpretation of ordinary NMR spectra. The third term allows for the direct interactions in the case of liquid crystal solvents. We denote the direct interactions by the constants D_{ij}. We note that D_{ij} is just twice B_{ij} which appears in the publications of Saupe and Englert.[1] By operating with the spin-Hamiltonian on an appropriate basis set of spin functions, one can generate the Hamiltonian matrix for the spin system. Proper linear combinations of spin functions diagonalize this matrix and correspond to stationary states of the spin system. Differences of eigenvalues correspond to resonant frequencies, and the linear combinations may be employed to compute intensities of the corresponding transitions. The NMR spectrum of a solute molecule may be accurately computer-simulated with the correct set of chemical shifts σ_i, indirect couplings J_{ij}, and direct couplings D_{ij}. An NMR spectrum analysis provides values for these constants, the interpretation of which may provide information on the solvent or solute. Our main interest here is in the direct coupling constants, D_{ij}, which are dependent on the geometry of the molecule through the equation

$$D_{ij} = -K\langle(3\cos^2\theta_{ij} - 1)r_{ij}^{-3}\rangle$$

Here r_{ij} is the length of the vector connecting nuclei i and j and θ_{ij} the angle between this vector and the direction of the applied field $\mathscr{H}_0$. K is a known constant and equals 120067 Hz Å^3 for protons. The angular brackets indicate that the enclosed expression must be averaged over the motions of the molecule. We shall here consider the molecule as rigid, that is we average over the molecular tumbling only. The influence of molecular vibrations is small and will be touched upon later.

In interpreting our D_{ij}, we shall assume that in a liquid crystal phase, a solute molecule finds itself in a cylindrically symmetrical environment.[1] The axis of cylindrical symmetry would constitute the optic axis in the local environment of the solute molecule. In a nematic phase, this optic axis probably corresponds to the direction of the long axis of the solvent molecules. It can be shown that if the solute molecules do find a cylindrically symmetrical environment, then we may write

$$D_{ij} = \tfrac{1}{2}\langle 3\cos^2\alpha - 1\rangle S_{ij} 2K_{ij}\langle r_{ij}^{-3}\rangle$$

where

$$S_{ij} = \tfrac{1}{2}\langle 3\cos^2\theta'_{ij} - 1\rangle$$

Here α is the angle between the local optic axis and the applied field direction. Saupe has defined the order parameter S_{ij} for the nuclear pair i and j in terms of the angle θ'_{ij} between the optic axis and the internuclear vector.

Alternatively we may define a cartesian coordinate system fixed in the molecule. Now a single order matrix $S_{\mu\nu}$ may be used to describe the orientation of the molecule relative to the optic axis.

$$S_{\mu\nu} = \tfrac{1}{2}\langle 3\cos\theta_\mu \cos\theta_\nu - \delta_{\mu\nu}\rangle$$

where

$$\mu, \nu = x, y, z.$$

Here θ_μ is the angle between the molecule fixed μ axis and the local optic axis, and $\delta_{\mu\nu} = 0$ if $\mu \neq \nu$, and $\delta_{\mu\nu} = 1$ if $\mu = \nu$.

The elements of this order matrix are related to the motional constants C, which are coefficients of 2nd degree spherical harmonics in an expansion of the probability of molecular orientations relative to the applied field.[8]

$$C_{3z^2-r^2} = 5^{1/2} S_{zz} \tfrac{1}{2}(3\cos^2\alpha - 1).$$

$$C_{x^2-y^2} = 5^{1/2} 3^{-1/2}(S_{xx} - S_{yy}) \tfrac{1}{2}(3\cos^2\alpha - 1),$$

$$C_{xz} = 5^{1/2} 3^{-1/2} 2 S_{xz} \tfrac{1}{2}(3\cos^2\alpha - 1),$$

$$C_{yz} = 5^{1/2} 3^{-1/2} 2 S_{yz} \tfrac{1}{2}(3\cos^2\alpha - 1),$$

$$C_{xy} = 5^{1/2} 3^{-1/2} 2 S_{xy} \tfrac{1}{2}(3\cos^2\alpha - 1).$$

The direct dipole-dipole interactions may be expressed as a sum of at most five terms, each of which is a product of a motional constant and a factor which depends only on the mean molecular geometry in the molecule-fixed coordinate system.

$$
\begin{aligned}
D_{ij}^{dir} = -2 \times 5^{-1/2} K_{ij} \Bigg\{ & + C_{3z^2-r^2} \left[\left\langle \frac{(\Delta Z_{ij})^2}{r_{ij}^5} \right\rangle_{Av} - \frac{1}{2} \left\langle \frac{(\Delta X_{ij})^2}{r_{ij}^5} \right\rangle_{Av} \right. \\
& \left. - \frac{1}{2} \left\langle \frac{(\Delta Y_{ij})^2}{r_{ij}^5} \right\rangle_{Av} \right] + C_{x^2-y^2} 3^{1/2} \left[\frac{1}{2} \left\langle \frac{(\Delta X_{ij})^2}{r_{ij}^5} \right\rangle_{Av} \right. \\
& \left. - \frac{1}{2} \left\langle \frac{(\Delta Y_{ij})^2}{r_{ij}^5} \right\rangle_{Av} \right] + C_{xz} 3^{1/2} \left[\left\langle \frac{(\Delta X_{ij})(\Delta Z_{ij})}{r_{ij}^5} \right\rangle_{Av} \right] \\
& + C_{yz} 3^{1/2} \left[\left\langle \frac{(\Delta Y_{ij})(\Delta Z_{ij})}{r_{ij}^5} \right\rangle_{Av} \right] \\
& + C_{xy} 3^{1/2} \left[\left\langle \frac{(\Delta X_{ij})(\Delta Y_{ij})}{r_{ij}^5} \right\rangle_{Av} \right] \Bigg\}
\end{aligned}
$$

Structure of the Solvent

We shall now consider the information which can be obtained on the nature of the solvent phase from the interpretation of mainly solute, but also some solvent, NMR spectra.

Consider first the proton NMR of nematic *p*-azoxyanisole shown in Fig. 1. The great (25,000 cps) width of the spectrum suggests that the solvent molecules are oriented with their long axes parallel to the applied field, and that the optic axis is also parallel to the field. The relatively narrow (200 Hz) peak-widths of this spectrum indicate that the solvent molecules are moving rapidly relative to one another. If they were fixed, line widths of many thousand Hz or more would be expected (as in the case of solids).

The spectrum of benzene dissolved in the nematic phase of *p,p′*-di-*n*-hexyloxyazoxybenzene given in Fig. 1 is several thousand Hz wide. It has been analyzed.[8] The dipole-dipole interactions determine its major structure. The presence of the D_{ij} shows that the benzene finds an anisotropic environment. The peaks are sharp with widths of order 5 Hz. This shows that all benzene molecules find an identical magnetic environment, on the average. Since the lifetime of proton spin states is of order 1 sec, it follows that the benzene must be moving quite rapidly through the solvent, so that intermolecular direct interactions average to zero. The indirect couplings affect only minor features of the spectrum, for example the position of the two small peaks at the center. From their position, and with the assumption that benzene protons lie on a hexagon, one may deduce that for a pair of protons ortho to one another the D_{ij} and J_{ij} are of opposite sign.[8] It is very probable that the ortho J_{ij} is positive; accordingly the ortho D_{ij} is negative. This implies that the plane of the benzene ring tends to be parallel to the applied field in the anisotropic environment of this nematic phase. An intuitive interpretation is that the solvent molecules have their long axes parallel to $\mathscr{H}_0$, and thus benzene fits best with its plane parallel to $\mathscr{H}_0$.

Recently Sobajima has reported NMR studies of methylene chloride in Poly-γ-benzyl-*L*-glutamate (PBLG).[9,10] The solutions are liquid crystalline at some concentrations,[11] one of these is 15.8 weight % polymer. Figure 2 shows the proton NMR of such

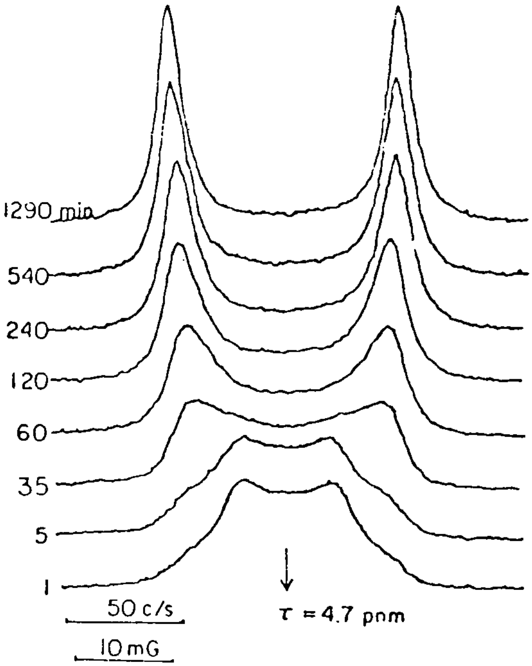

Figure 2. Variation of the methylene chloride doublet with time in a liquid crystalline solution with Poly-γ-benzyl-*L*-glutamate. (From: Sobajima, *J. Phys. Soc. Japan* **23**, 1072 (1967).)

a solution 1 minute after it was placed in the spectrometer and at a sequence of subsequent times. The spectrum of methylene chloride in an anisotropic medium consists of two peaks, which may be interpreted as the resonance of one proton in the dipolar field of the other. The initial spectrum of Fig. 2 is clearly a powder pattern; that is a spectrum corresponding to many regions with random orientations for the optic axis: the initial solvent is poly (liquid) crystalline. The final upper trace of Fig. 2 taken after 1290 min. is the spectrum of methylene chloride in a uniformly oriented anisotropic solvent. The fact that the peak positions coincide with the outer extremes of the initial powder pattern suggests strongly that the solvent optic axis is parallel to the applied field direction. The solutions are highly viscous; when the sample tube is turned in the spectrometer, the splitting exhibits the $(3\cos^2\alpha - 1)$ angular dependence, supporting the conclusion that the optic axis is parallel to the magnetic field in the solution oriented by the applied field.[9] We make the tentative conclusion that the long rod-like PBLG molecules have their long axes parallel to the applied field. This conclusion is supported by X-ray diffraction evidence.[9,10]

Cholesteric liquid crystals may be used as solvents in NMR experiments. As an example, we show in Fig. 3 the proton NMR of benzene in cholesterylnonanoate. All the peaks of the benzene spectrum can be observed, but they appear quite broad in the wings. Peaks in the center of the spectrum appear relatively more intense. The benzene spectrum stands on a shoulder of the cholesterylnonanoate spectrum. Our tentative understanding of this spectrum is that the solvent has not been aligned by the magnetic field even after exposure to the field for a few days. All local optic axis orientations appear to be equally likely.

In Fig. 4, we display the NMR of benzene in a compensated mixture of cholesteryl derivatives, cholesteryl chloride and myristate.[12] The pure derivatives have opposite macroscopic helicities. When mixed 1.9/1 by weight the mixture is almost nematic; in other words the helical pitch is almost infinite. The spectrum in Fig. 4 shows that this solvent presents a uniform

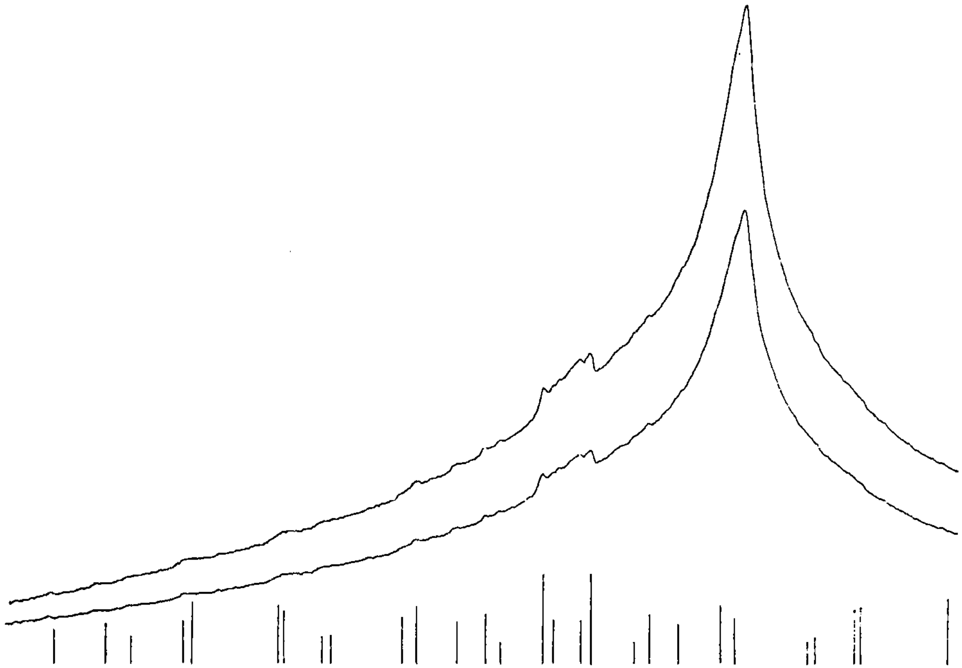

Figure 3. Proton NMR of benzene in cholesteryl nonanoate at 55 °C. Benzene peak positions and intensities are indicated by bars below experimental spectrum.

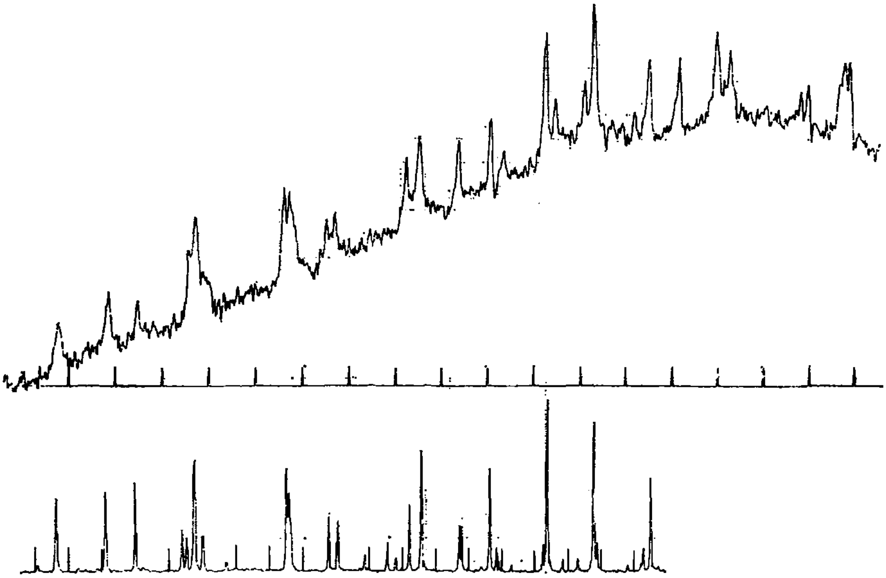

Figure 4. The top trace is the NMR spectrum at 40° of a mixture of 0.655 g of cholesteryl chloride, 0.344 g of cholesteryl myristate, and 0.01 g of benzene. The sharp lines are typical of the benzene spectrum in a nematic solvent. The very broad background resonance is due to the solvent. For comparison, the bottom trace gives a benzene spectrum in nematic hexyloxyazoxybenzene at 90°. Both traces cover a spectrum width of about 2 kHz. The center of the symmetrical benzene spectrum is midway between the two strongest lines; a number of lines at the high-field end of the spectrum are not reproduced. Frequency markers are 106 Hz apart; for the top spectrum they are given on the separate center trace, while for the bottom spectrum they are the sharp peaks superposed on the spectrum. (From: Sackmann, Meiboom and Snyder, *J. Am. Chem. Soc.* **89**, 5982 (1967).)

magnetic environment for the benzene. This suggests two possibilities: either the solvent is nematic; or it is cholesteric and the pitch axis is parallel to the applied field. The spectrum of benzene in this compensated solvent differs slightly from that in Fig. 1. Analysis shows that here the direct and indirect couplings of protons ortho to one another are of the same sign. This suggests that the plane of the benzene ring is perpendicular to the applied field direction. Since the long axis of cholesteryl molecules are believed to be perpendicular to the pitch direction, this would be intuitively consistent with the solvent being cholesteric with the helical axis parallel to the applied field. If the mixture were nematic with the long axis of solvent molecules parallel to $\mathscr{H}_0$, we would expect the opposite benzene orientation. These conclusions were confirmed by diffraction of monochromatic light from the compensated mixture oriented in a magnetic field. The pitch axis was found to be parallel to the applied field.[13] It is unclear at this time why the nearly compensated mixtures align in a magnetic field, while the pure cholesteryl nonanoate mentioned above does not.

It has been possible to show that the compensated mixture of cholesteryl derivatives presents a locally helical environment to solute molecules. In Fig. 5 is shown the proton NMR of racemic

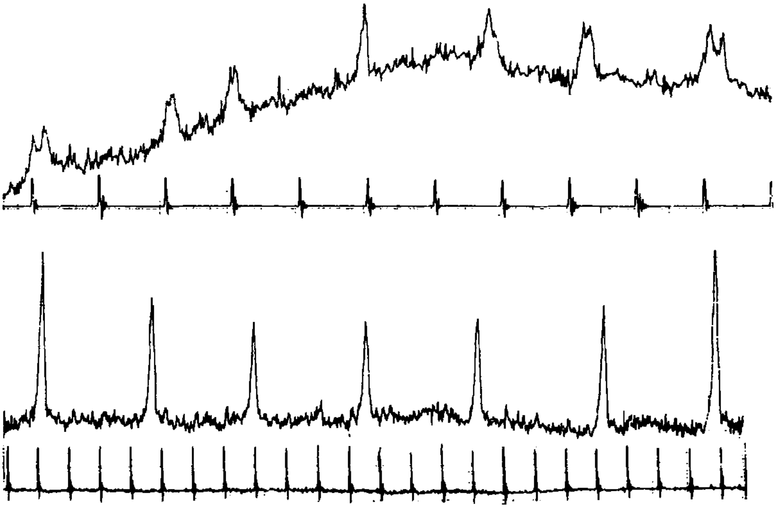

Figure 5. The upper trace gives the 60 MHz NMR spectrum at 40° of a mixture of 0.01 g of racemic 3,3,3-tri-chloropropylene oxide, 0.53 g of cholesteryl chloride, and 0.28 g of cholesteryl myristate. The very broad background is due to the solvent. The lower trace gives the spectrum of 0.01 g of racemic 3,3,3-trichloropropylene oxide in 0.1 g of *p,p'*-di-*n*-hexyloxyazoxybenzene at 90°. The trace below each spectrum gives frequency markers, spaced 106 Hz apart. (From: Sackmann, Meiboom and Snyder, *J. Am. Chem. Soc.* **90**, 2183 (1968).)

3,3,3-trichloropropyleneoxide.[14] The upper spectrum is in the compensated solvent, the lower in nematic, *p,p′*-di-*n*-hexyloxyazoxybenzene. A doubling of all peaks in the upper spectrum is evident. Analysis shows that the optical antipodes of the solute are each giving one component of the double peaks. We can consider the antipodes to be like right- and left-handed screws. They experience different forces, and thus orient differently in their helical environment.

A cholesteric liquid crystal can be prepared in another way: by adding an optically active component to a nematic phase.[15] We have done that by adding about 2% by weight of *p,p′*-di-active-amyloxyazoxybenzene to the *n*-hexyl-derivative.[12] At temperatures above 100 °C the NMR spectrum of benzene is identical to that of benzene in the nematic phase of *p,p′*-di-*n*-hexyloxyazoxybenzene: We assume the phase is nematic. Below 100 °C the spectrum of benzene disappears. The change is reversible. We believe that a transition to the cholesteric phase has occurred at the lower temperature. The helical axis is here presumably perpendicular to the applied field, with the long axis of solvent molecules perpendicular to the pitch axis. This orientation would be favored by the diamagnetic anisotropy of the solvent molecules. The sharp benzene spectrum is expected to disappear in this phase, because the orientation of the environment would vary for solute molecules at different positions along the pitch axis. The existence of this phase transition was also observed visually.[12]

Soap solutions have been employed as a solvent in NMR, with solute molecules giving highly resolved spectra.[16,17] These solvents are liquid crystalline at room temperature. They are specially suitable for dissolving polar molecules.

Structure of the Solute

Saupe and Englert noted that much information on molecular structure is available in the solute spectrum.[6] We have developed experimental and theoretical methods to facilitate the determination of molecular structure. There have been several determinations of structural parameters for small molecules reported.[18,19,20] Several careful studies are reported at this conference.[21,22] In this review we would like to outline the present status of this work with the example of bicyclobutane, the structure of which is outlined in Fig. 6.

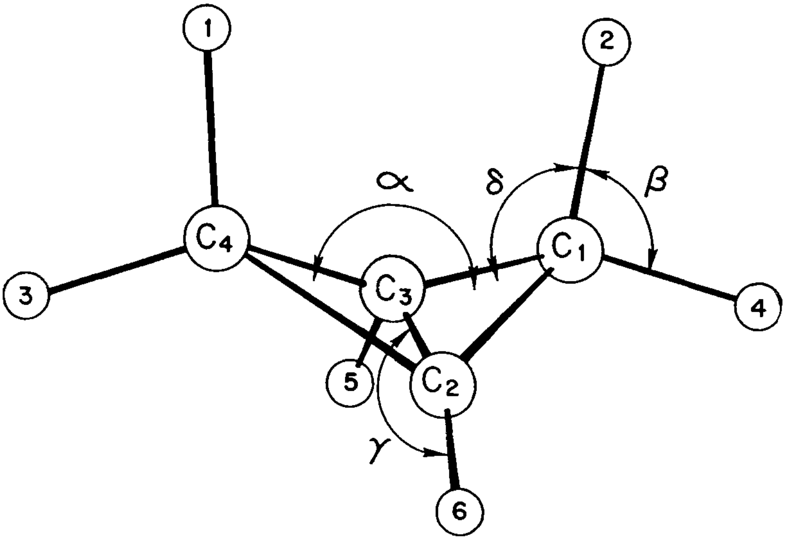

Figure 6. Bicyclobutane molecular model. (From: Meiboom and Snyder, *Science* **162,** 1337 (1968).)

The basic method of spectrum analysis is one of trial and error. We guess a set of motional constants and an equilibrium geometry to compute a set of D_{ij}. We must also assume a set of indirect couplings, J_{ij}, and shielding constants, σ_i. A computer program then takes care of setting up the Hamiltonian, and computing peak positions and intensities from it. By folding in a Lorentzian peak shape, with a width adjusted to correspond to the experimental one, the computer will simulate a realistic-looking spectrum. The initial spectrum fit is made visually until an assignment of peaks can be made. Then the fit is completed by computer variation of all or any subset of parameters for a least-square fit of the assigned peak positions. As the fit improves, more peaks are assigned and more parameters fitted.

As a special aid to making the visual fit, we have employed the Bell Labs " Graphic-1 " system, which permits the computation and immediate console display of theoretical spectra. This system has been a great help in small molecules such as cyclopropane for which only a small number of parameters need be varied. A visual fit for bicyclobutane was not achieved by this method even after 200 trials, and with a knowledge of the electron diffraction geometry. The reason for this difficulty is apparent. The number of parameters required to fit the bicyclobutane spectrum is large. Two constants are needed to describe the motion. Eight ratios of distances define the molecular shape, if (C_{2v}) symmetry is assumed. The chemical shifts of two kinds of protons relative to the third must be established. Seven distinct proton-proton indirect spin couplings must be fixed. The experimental proton NMR of bicyclobutane is the upper spectrum of Fig. 7. It contains about 250 lines. The line positions are quite sensitive to the parameter values and made the visual method of fitting and peak assignment practically impossible. This difficulty was overcome by a double resonance experiment. In this experiment a particular peak is observed, while the sample is irradiated at a second

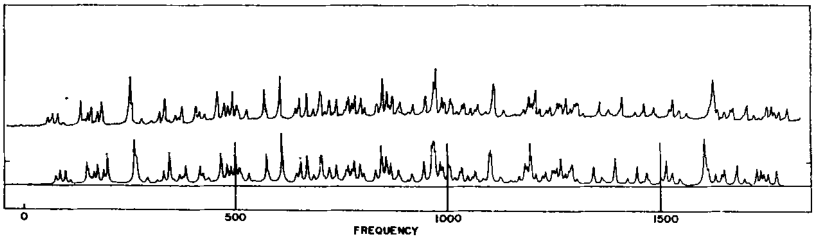

Figure 7. Spectrum of bicyclobutane. The top spectrum is theoretical, calculated with the parameters of Table 1. The bottom spectrum is experimental. (From: Meiboom and Snyder, *Science* **162**, 1337 (1968).)

frequency which is swept through the spectrum. Each time the second frequency passes a peak having a nuclear spin state in common with the peak being observed, the intensity of the observed peak changes. The record of the response of the observed peak as a function of the frequency of irradiation is sometimes called an INDOR spectrum. There is one INDOR spectrum for each peak in the ordinary NMR spectrum. The INDOR spectra usually contain only a few peaks with characteristic patterns of position and intensity, which depend only slowly on our several parameters. A visual fit of the double resonance spectrum can therefore be completed rather easily, and gave the necessary clues for an eventual fit of all peaks in the ordinary spectrum. This is illustrated in the lower theoretical spectrum of Fig. 7. The rms deviation of line positions is about .6 Hz for all lines in the spectrum.

By adding several thousand spectra of bicyclobutane, we were able to observe the weaker spectra due to the 2% of the molecules which contain ^{13}C at each of the two types of carbon atoms. The fit of these spectra permitted us to complete the structure determination by locating the carbon atoms relative to the protons.

Our final chemical shifts are listed in Table 1. It is noteworthy that the shift of the 5 and 6 protons relative to the 3 and 4 protons is of opposite sign to that found in the isotropic phase. This must reflect the anisotropy of the proton chemical shift tensors, infor-

TABLE 1 Spin Hamiltonian Parameters in Hz for Bicyclobutane in a Liquid Crystal Solvent

$\sigma_{H_1} = \sigma_{H_2} = +29.8$
$\sigma_{H_3} = \sigma_{H_4} = 0.0$
$\sigma_{H_5} = \sigma_{H_6} = -29.4$

$J_{H_1-H_2} = +2.0$	$D_{H_1-H_2} = -766.6$
$J_{H_1-H_3} = +0.0$	$D_{H_1-H_3} = +285.8$
$J_{H_1-H_4} = +0.6$	$D_{H_1-H_4} = -153.8$
$J_{H_1-H_5} = -0.1$	$D_{H_1-H_5} = +97.4$
$J_{H_3-H_4} = +4.9$	$D_{H_3-H_4} = -148.0$
$J_{H_3-H_5} = +2.8$	$D_{H_3-H_5} = -227.4$
$J_{H_5-H_6} = +7.5$	$D_{H_5-H_6} = +247.1$

mation not available in ordinary spectra. We list in Table 1 the proton-proton indirect spin couplings which we have found by this analysis. They deviate by about ± 3 Hz from those found in the isotropic phase: we consider this to be within the experimental error. An important advantage of the NMR spectra in liquid crystal solvents is that a definite assignment of the indirect couplings can be made; their signs are also correctly determined relative to those of the motional constants. Also included in Table 1 are the D_{ij} values. They are large compared to the indirect couplings.

TABLE 2 Structure of Bicyclobutane

Coordinate	NMR	Electron Diffraction‡
$\angle\alpha$	120.2 ± 2°	122.8°
$\angle\beta$	110.2 ± 1°	116.0°
$\angle\lambda$	128.0 ± 2°	125.5°
$\angle\delta$	126.3 ± 1°	~ 122°
C1–C2	(1.507)	1.507 Å
C2–C3	1.507 ± .07	1.502 Å
C1–H2	1.167 ± .02	~1.106 Å
C1–H4	1.194 ± .02	~1.106 Å
C2–H6	1.142 ± .02	1.108 Å

‡ Reference 23.

The bicyclobutane geometry we find is given in Table 2. It is compared there with an unpublished electron diffraction structure by Bastiansen.[23] The C1—C2 bond has been assigned its electron diffraction length.[24] The large uncertainty in the C2—C3 bond length as determined by NMR is the result of the small dipolar interactions of ^{13}C at the C2 position with protons other than the one directly bonded to it. This causes the effect of these interactions to fall in a region obscured by the NMR of bicyclobutane containing no ^{13}C. In general the agreement of the two structures is rather good. We believe the discrepancies are mainly due to the fact that we have not yet taken account of the effect of vibrations, but have only found the best fixed geometry. In general, in cases where results of other methods are available and a comparison possible, our NMR studies find C—H bonds rather too long relative to C—C bonds.[25,26] This is in part due to the large anharmonicity of the C—H bond. We also note that in our analysis, the protons are located relative to one another first, then the carbons fixed relative to the protons.

We are optimistic that NMR of molecules in liquid crystal solvents will be a useful means of determining molecular structure.[27]

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